THIOCYANATIONS VII: SOLVENT INDUCED EFFECTS IN IODINE (I) THIOCYANATE-ALKENE REACTIONS

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Iodine (I) thiocyanate has received little attention in the past as an electrophilic reagent for olefin addition.[1] Recently, however, the products of ISCN addition to aromatic olefins carried out in polar solvents have been reported.[2] The only available information on this reaction with aliphatic olefins in solvents of varying polarity is represented by the formation of episulfides that were prepared via ISCN without isolation of the intervening adduct[3] and by titrimetric analysis of excess reagent following addition of the presumed ISCN reagent.[4,5] None of the reported aliphatic olefin studies[3-5] offers insight or firm evidence into the nature of the products, purportedly the α-iodo-β-thiocyanate adducts,[4c] and mechanism.

In this paper, we report the products of ISCN addition to cis- and trans-3-hexenes, model systems chosen as convenient representatives of aliphatic internal olefins. The products thus permit the presentation of a mechanism in comparison with that established for thiocyanogen[6] and thiocyanogen chloride[7,8] additions. The ISCN reagent was generated via the equilibrium (eq 1)[4,9] in two separate solvents, benzene (nonpolar) and acetic acid (protonic polar), since thiocyanogen type reactions were reported earlier to be solvent dependent[6,8] and because these solvents were employed in the former analytical[4] and kinetic[5] studies. An essential consideration in the mechanism is whether the intermediate (or transition state) involves either the iodonium cation 1

$$I_2 + (SCN)_2 \rightleftharpoons 2ISCN \qquad (1)$$

(eq 2a) with resultant formation of adducts 3 and 4 through the ambident thiocyanate anion or the epicyanosulfonium cation 2 (eq 2b) to give exclusively adduct 3. Thiocyanogen and thiocyanogen chloride additions are both known to proceed through a type 2 intermediate as shown in eq 3a and 3b below.[6-8] The equations 2 and 3 illustrate additions to a trans olefin to give erythro products, whereas the corresponding cis olefin gives threo products.

In the experiments carried out in benzene, ISCN was prepared by Raby's procedure.[4] Two products were isolated from the separate reaction of each olefin in benzene, an iodoisothiocyanate

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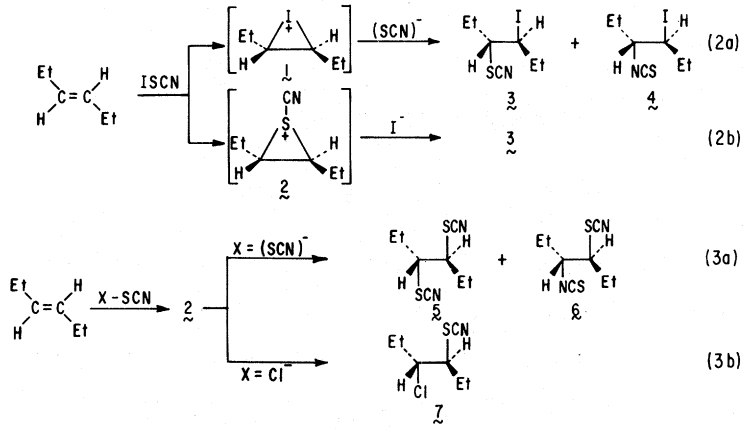

4 (eq 2a) and an isothiocyanatothiocyanate 6 (eq 3a) (Table 1). Doubling the ISCN/olefin ratio from 1.2 to 2.4 had little effect on product distribution. Ferric thiocyanate, which profoundly influences the product makeup of thiocyanogen additions,[6a] had no effect on the product outcome in the ISCN experiments. Product 4 was isolated by preparative GLC and its structure and stereochemistry were identified by GLC, IR (2060 cm^{-1} broad for -NCS), PMR, and mass spectrometric analysis (M^+ 269). Compound 6 was isolated in a similar manner and characterized by comparison of its physical constants with those of the known[6a,b] compound. Adducts 4 and 6 from trans-3-hexene had erythro configurations and were stereochemically pure. In similar fashion, cis-3-hexene gave essentially the same product distribution as that shown in Table I except that adducts were of threo configuration. The methine coupling constant order for the erythro adduct 4 (J_{av} = 5.4 Hz) and the threo adduct (J_{av} = 2.4 Hz) corresponded with that of other vicinal isothiocyanate pairs.[10] Conversion of each olefin to products was quantitative. Unlike the thiocyanogen and thiocyanogen chloride reagents, these results establish that ISCN is not the exclusive reactive species in benzene solution. Although the equilibrium (eq 1) in benzene favors ISCN formation, at least 10% thiocyanogen must be present based on the product distribution (Table I). Because both ISCN and $(SCN)_2$ are present in solution, formation of 6 arises from the pathway outlined in eq 3a (through intermediate 2), whereas 4 is formed via an independent pathway as shown in eq 2a. Stereospecific formation of adduct 4 suggests that the cyclic iodonium ion[11,12] does not engage in ring opening prior to attack by the thiocyanate anion. Neither iodothiocyanate 3 (eq 2a) nor vic-dithiocyanate 5 (eq 3a) products that would arise by attack of the sulfur end of the thiocyanate ion on intermediates 1 (eq 2a) or 2 (eq 3a), respectively, were detected in the product mixtures from either olefin. Woodgate et al[2]

TABLE I

REACTION OF IODINE (I) THIOCYANATE WITH trans-3-HEXENE: SOLVENT AND IRON CATALYST EFFECTS

	erythro PRODUCT,[a] %			
Solvent[b]	I NCS 4	SCN NCS 6	NCS SCN 5	NCS OAc 8
Benzene	94(91)[c]	6(9)[c]		
Benzene-Fe Catalyst	95	5		
Acetic Acid[d]		20	74	6

a)All products were stereochemically pure; b) Experimental conditions for 2.4 mol ratio of ISCN/olefin: Iodine (24 mmole), thiocyanogen (24 mmole), and olefin (10 mmole) in 80 ml solvent; c) Values in parenthesis are from reaction with 1.2 mole ISCN/mol olefin; d)Results of varying the $I_2/(SCN)_2$ ratio in the range 4:1 to 1:1 (formation of ISCN via eq 1) were comparable.

examined the products of addition of ISCN to aryl alkenes. In their study, the ISCN was generated from I_2 and KSCN in chloroform and sulfolane. They also observed the formation of adducts such as types 5 and 6 under these conditions but attributed their occurrence to attack on 4 by the ambident thiocyanate anion with resultant displacement of iodine. In Woodgate's[2] work in which ISCN is generated via an ionic pathway and presumed free of thiocyanogen, it is possible for the equilibrium (eq 1) to be an important component of the reaction in polar solvents. Formation of thiocyanogen in the equilibrium would account for Woodgate's products corresponding to types 5 and 6 and would thus offer an alternate explanation for the occurrence of noniodo products. Woodgate et al[2] also had found TlSCN to be a catalyst in chloroform and sulfolane solutions for the preferential, though not exclusive, formation of iodoisothiocyanate adducts. In our work in benzene solution, formation of 4 arises as the sole iodo and near exclusive product, indicating thallium catalyst to be unnecessary.

The exclusive formation of one iodo isomer, the iodoisothiocyanate 4, thus supports 1 and excludes 2 as the intermediate species for the generation of iodoisothiocyanate adducts in benzene. The possibility of  as the intermediate was previously rejected in olefin-thiocyanations on grounds that no diisothiocyanate adduct was detected in product mixtures, which eliminates the possibility of adduct 6 arising through prior formation of 4.[6,13] In the thiocyanogen halide series, the difference in mechanism between ClSCN (eq 3b) and ISCN (eq 2a)

additions is attributed to opposite polarizations of the halogens in the manner $Cl(\delta^-)$-$SCN(\delta^+)$[7] and $I(\delta^+)$-$SCN(\delta^-)$[1b], a proposal which is supported by the present results.

A series of experiments was also conducted in which ISCN was generated in the same manner as previously described for benzene, except that the solvent medium employed was acetic acid. Attempted additions of ISCN to cis- and trans-3-hexene in this solvent, in contrast to those carried out in benzene, yielded no reaction products containing iodine. Instead, the only products formed in the reaction were those normally derived from thiocyanogen addition to the olefins, i.e., vic-dithiocyanate 5, α-isothiocyanato-β-thiocyanate 6 and α-acetato-β-thiocyanate 8 adducts (Table 1).[6a] The acetate adduct is obtained through solvation of 2.[6a] Changes in the mol ratio of $I_2/(SCN)_2$ did not change the composition of the product mixture. These results suggest that little, if any, ISCN is generated in the equilibrium (eq 1) in acetic acid solution, which would preclude formation of iodonium intermediate 1 (eq 2a). Therefore, in acetic acid, only thiocyanogen is primarily present for addition via pathway 3a. Interpretation of the kinetics of ISCN-olefin reactions carried out in acetic acid by other investigators[4,5] are therefore brought into question, since their data actually represent the addition of thiocyanogen and not of ISCN.

REFERENCES

1. M. N. Hughes in "Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives", Ed. A. A. Newman, Academic Press, New York, NY, 1975, (a) p. 25; (b) p. 9.
2. P. D. Woodgate, H. O. Lee, and P. S. Rutledge, Tetrahedron Lett., 1531 (1976).
3. J. C. Hinshaw, Ibid., 3567 (1972).
4. (a) C. Raby, Ann. Chim., 6, 481 (1961); (b) C. Raby and P. Mesnard, Bull. Soc. Pharm. Bordeaux, 106, 13 (1967); (c) C. Raby,, J. Buxeraud, and J. Claude, Ann. Chim., 1, 65 (1976).
5. V. G. Collin et al., J. Prakt. Chem., 311, 238 (1969).
6. (a) R. J. Maxwell, L. S. Silbert, and J. R. Russell, J. Org. Chem., 42, 1510 (1977); (b) R. J. Maxwell, G. G. Moore, and L. S. Silbert, ibid., 42, 1517 (1977).
7. R. G. Guy and I. Pearson, J. Chem. Soc., Perkin Trans., 2, 281 (1973).
8. R. G. Guy and I. Pearson, Ibid., 2, 1359 (1973).
9. M. J. Nelson and A. D. E. Pullin, J. Chem. Soc., 604 (1960).
10. R. J. Maxwell, P. E. Pfeffer, and L. S. Silbert, J. Org. Chem., 42, 1520 (1977).
11. A. Hassner, M. E. Larber, and C. Heathcock, J. Org. Chem., 32 540 (1967); A. Hassner and F. W. Fowler, Ibid., 33, 2686 (1968).
12. F. Freeman, Chem. Rev., 75, 457 (1975).
13. L. S. Silbert, J. R. Russell, and J. S. Showell, J. Am. Oil Chem. Soc., 50, 415 (1973).